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The Heat of Dilution of
Methyl Alcohol Solutions

Chemical Engineering

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**THE HEAT OF DILUTION
OF
METHYL ALCOHOL SOLUTIONS**

BY

EDWARD NEAL CHAPMAN

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Edward N. Chapman

ENTITLED THE HEAT OF DILUTION OF SOME METHYL ALCOHOL
SOLUTIONS.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

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INTRODUCTION.

Part I.

The main purpose of this thesis is to determine accurately the heat of dilution of Methyl alcohol solutions. Approximately four normal solutions of about 9,500 grams weight are used, and are diluted with from 200 to 400 grams of water. The rise in temperature, due to the addition of such a comparatively small amount of water, is very small. It is therefore essential that a sensitive and accurate thermometer be used. For this work a twenty five ohm platinum resistance thermometer, which will be described in detail later, is employed. The adiabatic calorimeter used is electrically controlled and was designed in connection with the thesis of Irving Randolph Ruby. It has a decided advantage over any other previous calorimeter as will be explained later. The strength of solutions are determined with an interferometer², which may be made to give an accuracy of one hundredth of one per cent.

T. W. Richards³ and his associates have completed some excellent calorimetric work, using an adiabatic calorimeter in which the water surrounding the calorimeter, (hereafter designated as "surroundings") and the calorimeter are kept at the same temperature. This insures that there will be little exchange of heat during a run, but corrections for stirring, evaporation, etc., have to be made. In the calorimeter used in this work no corrections are necessary, for the effects of stirring, etc. are balanced by a constant difference of temperature between the surroundings and solution. Richards used a very sensitive mercury thermometer in

his experiments, and has not favored the use of resistance thermometers. With proper care however the possibilities of resistance thermometers far exceed that of the mercury as regards both efficiency and sensitiveness. W. P. White ⁴ has written several articles in regard to the advantages of thermo-elements for calorimetric work and has found them to be highly satisfactory when proper precautions are taken. Dickenson and Mueller ⁵ used the resistance thermometer with apparent success. Steinwehr and Von Jaeger⁷ in their work on the calibration of a bomb calorimeter have also obtained satisfactory results with a resistance thermometer.

EXPERIMENTAL.

Description of Calorimeter Used.

Part II.

As stated before the calorimeter used, with a few slight modifications, is as described in Mr. Ruby's thesis and a detailed description may be obtained from his thesis. The solution compartment, or calorimeter proper, has a capacity of ten liters and contains a dilution cup with a capacity of one-half litre. The bath around the calorimeter is heated by means of electrical energy, (the heater is attached to the stirring apparatus) and a fourteen junction manganin-copper thermo-couple measures the difference between the solution and "surroundings." Adequate means of stirring are provided as it is necessary to bring both quickly to a uniform temperature throughout. A second external bath is provided in case the room temperature be too high, for if it were not present the temperature of the "surroundings" could not be kept as low as necessary. The temperature of the solution is measured by a platinum resistance thermometer, and the changes in resistance are determined by a Leeds and Northrup wheatstone bridge. With careful handling $1/100,000$ of an ohm can be measured accurately. The solution heater for the determination of the heat capacity of the calorimeter consists of a coil of copper tubing through which is run a manganin wire carrying the current. A Leeds and Northrup potentiometer is used in determining the electrical energy passed into the calorimeter compartment. The electromotive force is obtained by measuring the potential drop across a definite part

of a known high resistance connected as a parallel circuit, while the current value is found from the drop across a constant resistance connected in series. These electromotive force values are compared against a standard cell 6 in connection with the potentiometer.

Theory of Manipulation.

A certain amount of water when added to a methyl alcohol solution causes a definite rise in temperature, and this rise changes the resistance of the resistance thermometer. The change in resistance is obtained by actual measurement. A measured amount of electrical heat energy is then passed into the calorimeter, and the rise is determined as before. By a simple proportion the amount of heat evolved due to the dilution can be easily computed. Thus the resistance thermometer acts only as a sensitive thermoscope and its calibration is unnecessary, provided its temperature coefficient of resistance is constant within the range of the temperature used. Radiation losses are taken care of by keeping the "surroundings" enough lower than the calorimeter so that the heat exchange from the calorimeter to the "surroundings" will just compensate for the evaporation and heat evolved by stirring in the calorimeter. When this condition is reached the temperature reading (resistance thermometer reading) remains constant. Since the heat capacity is constant in both determinations it is eliminated in the process of calculation.

Changes made in Calorimeter.

Much trouble was experienced in procuring a resistance ther-

mometer which would give the desired results. In order to be of value the thermometer must be very sensitive to minute changes in temperature and not too fragile in construction. The thermometer first tried ("Thermometer A"), which was made by Leeds and Northrup from a design furnished by the Bureau of Standards, consisted of a platinum coil wound on a mica strip over which was placed a platinum sheath. This sheath was fastened securely to a glass tube holding the two compensating leads and the leads to the platinum wire. The leads were passed through an enlarged top sealed and packed with P_2O_5 to keep the interior air and water tight. This thermometer lost its effectiveness gradually upon use and regained it again after laying aside for some time. This was probably due to the entrance of moisture which caused a leakage of current from the thermometer to the solution by breaking down the insulation. Attempts were made to seal it with "Bakelite" but the thermometer was finally set aside, for outside currents, as from the heater, affected it. The last disturbance mentioned was diminished by grounding the calorimeter.

Another thermometer ("thermometer B") with about the same internal resistance (25 ohms) was made. It consisted of a coil of platinum wire wound on a glass rod onto which was fused a glass tube. The glass used had the same coefficient of expansion as the platinum wire. A larger tube containing the leads was attached to the fused portion in a manner quite similar to "thermometer A". As the portion containing the platinum coil was completely sealed off from the upper section no means for drying was necessary although a small P_2O_5 bulb was attached.

This thermometer being much better insulated did not have the electrical leaks as "thermometer A" and the galvanometer accordingly acted with its full sensitivity. The thermometer, however, showed only half the change in resistance than "thermometer A" for approximately the same rise of temperature. The platinum wire used in "thermometer B" might not have been pure, thus affecting the change in resistance due to a given rise in temperature. Any jar changed the resistance considerably and there was no marked tendency for the galvanometer to come back to the former reading before the disturbance. "Thermometer A" also was affected by any appreciable jar.

A third thermometer ("thermometer C") was then made similar in construction to "thermometer B" differing only in that the platinum coil was wound loosely, and a small air space was left between it and the glass tube covering. As the lower section was sealed off from the upper part no drying material was necessary. Using this thermometer, the galvanometer had its full sensitivity, but a large lag effect was present due to the air space around the platinum wire. "Thermometer C" was even more sensitive to jars than "thermometer B" and the change in resistance due to a given rise in temperature was practically the same, therefore "thermometer B" was used in the determinations.

Experiments were made upon the best means of allowing the dilution to take place, and how to remove the stopper in the cup containing the water for dilution, without disturbing the thermometer. It is evident that the dilution should not take place too rapidly or else the temperature difference between the calorimeter and "surroundings" cannot readily be kept constant. This

is due to the fact that a lag in the galvanometer reading of the differential thermometer has to be allowed for. The dilution will take place slowly if the level of the solution and dilution water are the same. 300 grams of water brought the levels to the same height when 9,500 grams of alcohol solution were used. As soon as the temperature ceased to rise the cup was lowered so that the dilution would be complete, for then the stirring caused vigorous circulation through the cup. Because of the sensibility of the "thermometer B" to jars it was necessary that the rubber stopper in the bottom of the dilution cup should be pushed out without disturbing the thermometer. Tin foil, wrapped smoothly over the stopper aided greatly for it prevented the swelling of the rubber by the alcohol. This simple arrangement works very well and no disturbance can be noted by the galvanometer readings.

It is essential that the rate of stirring remains constant throughout the entire run and considerable trouble was experienced in procuring this condition. A direct belt drive from an inch pulley to a large wheel gave a steady and quiet motion,, but machine gears are to be recommended. A speed of from 60 to 65 revolutions per minute is sufficient, but any less is undesirable on account of the difference in temperature throughout the water of the "surroundings" caused by an unequal stirring affect. There is a tendency for the upper portion to remain at a higher temperature for a time.

Part III. Description of a Run for the Determination of the Heat of Dilution.

The heat of dilution is determined at 25° C and an approximate four-normal methyl alcohol solution is used. About 9,500 grams of alcohol solution is employed for each determination and is diluted with 300 grams of distilled water. Some hours previous to the run the solution, water for dilution, and the water for the "surroundings," are allowed to come to constant temperature (25° C.) in a thermostat. The solution is weighed to within the nearest gram while the water for dilution is weighed to the nearest 0.01 gram, thus there will be no error in weighing of over 0.01%. Any further accuracy would be useless for some of the other readings give much less than that. The top of the calorimeter is clamped down tightly and then the water for the "surroundings" is poured around and over the calorimeter to the depth of one-half inch. The alcohol solution and water for dilution are then poured through tubes into the calorimeter and dilution cup respectively, and the stirring commenced at once. By means of the heater, located in the stirrer for the "surroundings," the galvanometer reading for the differential thermometer is then adjusted until the resistance thermometer reading remains constant for several minutes. When this condition is reached the tendency for the solution to heat up due to the stirring action is just balanced by the radiation outward to the "surroundings" which are slightly lower in temperature. Any effect from evaporation is taken care of also in this manner.

When the room is warm it is necessary to keep the extreme outside bath much colder than the "surroundings" in order to keep the temperature down. If the temperature difference between the calorimeter and "surroundings" tends to increase the heater, contained in the stirrer, is used to warm the "surroundings" till the proper difference be restored. It is necessary to keep the difference in temperature constant through out the run.

After a constant temperature of solution has been reached the stopper is forced out of the dilution cup and the dilution completed as described earlier in this paper, care being taken to follow the rise in temperature with the heater for the "surroundings" so as to keep the temperature difference between the solution and "surroundings" constant. Readings on the temperature of the solution are then made.

Immediately after the temperature has become constant following the dilution, a measured amount of electrical energy is passed through the heater in the calorimeter. The heating is carried on until a considerably larger rise than that due to the dilution is obtained. Very accurate (to $< .01\%$) readings on the voltage and amperage are taken as often as possible while the time of heating is determined by means of a stop-watch. Usually the current is allowed to pass through the heater for about ten minutes, and the time measured to $1/5$ of a second, giving an accuracy of $.01\%$. The temperature rise is then determined as in the case of the dilution, only more time is required for the temperature to become constant because the heat generated in the heater is not conducted to the solution immediately. Now since,

the amount of heat, which can be determined from electrical energy, passed through the solution gives a certain change in resistance of the resistance thermometer, then by direct proportion the heat of dilution of the solution, caused by the addition of water, can be calculated. It is unnecessary to calibrate the thermometer or determine the heat capacity of the calorimeter for the values thus obtained are constant in both determinations, since during the entire run the specific heats and the temperature coefficient of resistance of platinum do not vary enough to affect the accuracy of the results.

Part IV. Determination of the Strength of Solution.

For determining the strength of solutions the Zeiss Interferometer is made use of. The manipulation of this instrument has been described in detail in a recent article by L. H. Adams.² A quantity of methyl alcohol (purified by refluxing with KOH and distilling from lime in a stream of hydrogen) is kept under a reducing atmosphere for use in these determinations. The strength of the solution in question is first roughly determined by means of specific gravity and then two solutions of known strength, one above and one below the unknown, are prepared by accurately weighing the water and purified alcohol. The shift of the fringes⁸ caused by the two known solutions is found and by comparing the shift produced by the unknown solution with either of the known solutions data is obtained from which interpolation gives the strength of solution directly.

Part V. Determination of Temperature Coefficient
 of "Thermometer B."

This determination is unnecessary for calculating the results of a run but gives a definite idea as to the change in resistance due to the rise of 1/10,000 of a degree.

Temperature	Resistance.
28.13	25.55012
<u>24.03</u>	<u>25.32970</u>
4.10	.22042

Thus 1/10,000 of a degree changes the resistance .0000056 ohm and since the ohm reading can be determined accurately to the fifth place the temperature is measured with precision to 2/10,000 of a degree.

Part VI. Determination of Resistance used for Pro-
 curing Amperage Values.

The resistance was determined by means of a Leeds & Northrup standardized Wheatstone bridge using the ratio arms of 1 to 1000 and 1 to 10,000.

Ratio 1 to 1000		1 to 10,000
Resistance with Connections	.1378	.1378
Resistance of Circuit	<u>.0048</u>	<u>.0048</u>
Resistance	.1330	.1330

The accuracy is evidently within 1/10 of 1%

Part VII. Relation of Temperature Difference to
Readings of Differential Thermometer.

The brass tubes of the thermocouple were placed in two baths of known temperature and the deflection due to the difference in in temperature observed. A deflection of one millimeter represents a difference of $.003^{\circ}$ C.

Part VIII. Typical Run.

The typical run on the following page is a fair representative of the determinations made. The temperature difference in centimeters on the galvanometer scale (column C) is evidently too high at first although some irregularity in the temperature reading (column B) is due to the fact that the solution has not been stirred long enough. At 4.8 centimeters difference the temperature reading of the resistance thermometer becomes constant. Very little time elapsed after dilution before the temperature reading became constant, but after the electrical energy is passed into the solution a longer time is usually necessary.

A	B	C	D	E	
	25.72				
1.47	.05140	5.9			
1.48	.05124	5.5			
1.49	.05111	5.4			
1.50	.05114	5.0			
1.51	.05126	5.0			
1.53	.051255	5.0			
1.54	.051255	5.1			
1.57	.051245	5.0			
1.58	.05123	5.0			
1.59	.05123	4.95			
2.00	.05121	4.7			
2.02	.05120	5.0			
2.06	.05120	5.0			
2.09	.05116	5.0			
2.11	.05116	4.8			
2.12	.05116	4.8			
2.13	.051155	4.7			
2.14	.05116	4.8			
2.15	.05116	4.8			
2.17	.05388	4.9			
2.20	.05389	4.8			
2.21	.053885	4.8			
2.22	.05389	4.8			
2.24			.32055	.32093	
2.25			.32035	.32130	Time
2.26			.32017	.32122	
2.265	Heating period		.31966	.32075	10 min.
2.275			.32046	.32020	
2.30			.32045	.32023	45-1/5
2.35			.32085	.32215	sec.
2.35	.06725				
2.36	.06726				
2.37	.06727				
2.38	.06725				
2.39	.06726				

A - Time in minutes

B - Resistance readings from resistance thermometer.

C - Temperature difference from thermocouple

D - Voltage readings on potentiometer in centimeters on galvanometer scale.

E - Amperage readings on potentiometer in centimeters on galvanometer scale.

Part IX. Analysis of Sample Solution.

Preparation of known solutions.

	No. 1	No. 2.
Weight water	49.505	49.457 grams
Weight alcohol	7.098	7.784
% Strength	12.539	13.598

Analysis by interferometer.

Zero reading (water on both sides)	=	30.
Temperature throughout	=	24.87° C.
No. 1 on right No. 2 on left	=	130.
No. 1 on right Unknown sol. on left	=	90.

Calculation of Strength of Solution.

$$(13.598 - 12.539) \times 60/100 = .637$$

$$\underline{12.539}$$

$$13.176 = \text{Strength of solution.}$$

Part X. Calculation of the Heat of Dilution of Run No.4.

The heat of dilution, expressed in joules, is determined from the following formula.

$$H = \Delta t \times \frac{E_p}{C_1} \times \frac{I_p}{C_2} \times T$$

H = heat of dilution (expressed in joules)

Δt = change of resistance, as measured by resistance thermometer reading, divided by corresponding change due to the electrical heat energy added.

E_p/C_1 = The actual value of the E.M.F. across the heater. E_p is the reading on the galvanometer obtained when the potential drop across a known high resistance connected as a parallel circuit to the heater is measured. C_1 is equal to 9434/434 which is the ratio of the two known resistance arms of the potentiometer. E_p/C_1 , therefore gives the actual E.M.F. across the heater for the resistance of the heater and line may be neglected when compared with the high resistance across which the E.M.F. is measured.

I_p/C_2 = the current passed through the heater. C_2 is a known resistance (.1330 ohms) in series with the heater and I_p is the potential drop across this resistance; therefore is the current in the heater circuit.

T = the time during which the electrical energy is applied (expressed in seconds.)

$$H = \frac{.00272}{.01337} \times .32043 \times \frac{9434}{434} \times \frac{.32097}{.1330} \times 645.2$$

$$= 2205.63 \text{ Joules.}$$

Results of four determinations as calculated from the above

formula:-

	No. 1.	No. 2.	No. 3.	No. 4.
Solution used	9504.	9498	9504	9487 grams
Strength of Solution	13.106	13.106	13.174	13.174%
Water used for dilution	297.7	299.93	399.74	400.21 gms.
Heat of dilution	1749.4	1735.7	2234.26	2205.63 joules

% difference between run No. 1 and run No. 2. = .784%

% " " run No. 3 and run No. 4. = 1.28 %

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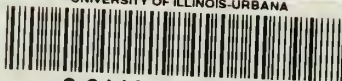
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